



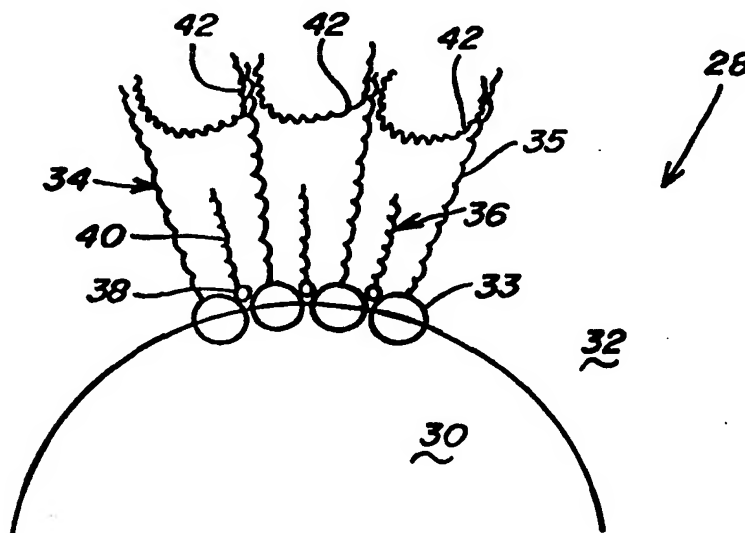
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(54) Title: **NANOSTRUCTURED AQUEOUS FUELS**

(57) Abstract

A thermally and temporally-stable water-in-fuel emulsion having micelle size less than 100 nm, and including water in an amount of at least 8 wt.% is provided. The emulsion, when burned as a fuel in an internal combustion engine, exhibits efficient combustion with significantly reduced soot output.



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NANOSTRUCTURED AQUEOUS FUELS

Field of the Invention

The present invention relates to multi-phase aqueous/nonaqueous compositions, and more particularly to a water-in-oil emulsion useful as a fuel.

Background of the Invention

The use of water as an additive in combustible fuels has been the subject of a significant amount of research and development. The addition of water to fuel reduces the overall temperature at which combustion of carbonaceous fuels takes place by acting as a heat reservoir. The reduction in temperature of combustion can reduce the emission of pollutants such as nitrous oxides and unburned hydrocarbons (soot).

Some arrangements have involved addition of aqueous mist to the intake manifold of internal combustion engines. While this can have the effect of reducing the temperature of combustion, this technique requires auxiliary fuel intake arrangements and does not result in optimal mixing of fuel and water. Therefore, the most interesting efforts to date have dealt with formulating mixtures of fuel, water, and emulsifier (surfactant), in an effort to relatively evenly disperse the fuel or water phase in the other phase to achieve good mixture. These mixtures can be of the water-in-oil or oil-in-water types, depending upon which phase is entrapped in the other (which phase forms micelles within a continuous phase defined by the other). In the formation of micelles, surfactant molecules arrange themselves as a layer with polar portions facing in one direction and non-polar portions facing in the opposite direction, the polar portions arranged adjacent a water phase and the non-polar portions arranged adjacent a fuel phase. In water-in-oil emulsions, isolated regions of water are surrounded by surfactant molecules which separate the water from a continuous, oil phase. In oil-in-water emulsions, the reverse exists, namely, isolated portions of oil are formed, surrounded by surfactant molecules which separate the oil from a continuous, aqueous phase.

The type of water/fuel aggregate formed (oil-in-water or water-in-oil) depends upon several factors that are known, and the formation of water-in-oil emulsions is somewhat challenging in that a surfactant or mixture of surfactants must be used whose ratio of hydrophilic to lipophilic portions matches the HLB of the desired water-oil ratio, while the solubility of the surfactants in water in this case must be low to induce the formation of a continuous oil phase.

Selection of suitable surfactants for water-in-oil emulsions therefore is non-trivial. In addition, in order to provide for an economically-viable fuel mixture, the amount of surfactant employed must be relatively small.

The task of creating commercially-viable, effective, water/oil mixtures as fuels is
5 challenging. The patent literature contains reports of water/oil mixtures as fuels, and a brief description of representative reports follows.

U.S. Patent No. 4,877,414 (Mekonen) describes use of certain types of mono olefin
(alpha olefin) compounds in relatively minor amounts in water-fuel-surfactant mixtures. Water
is preferably present at a level of from about 5% to about 25% by weight. Mekonen
10 hypothesizes that the mono (alpha) olefinic additives (and/or alkyl benzene additives) provide good results in that they in some way initiate or promote reactions analogous to cracking during the combustion of the fuel composition, producing smaller, lower molecular weight hydrocarbons known to be more readily combustible.

U.S. Patent No. 5,156,114 (Gunnerman) describes an aqueous fuel including about 20-
15 80% by volume water that purportedly produces approximately as much power as a similar volume of gasoline. A hydrogen-producing catalyst is included, and is believed to act as a catalyst for the dissociation of water molecules during ignition, releasing hydrogen and oxygen which increases the amount of energy delivered by the fuel.

U.S. Patent No. 4,804,495 (Bouchez) reports a heavy hydrocarbon/water multiple
20 emulsion having an internal phase that is a water-in-hydrocarbon emulsion and an external phase including water containing a surfactant which defines a continuous phase within which the internal phase is emulsified. The mixture is reported to include about 20-30% water with water droplets of the internal emulsion being on the order of 1-5 microns in dimension.

U.S. Patent Nos. 4,565,588, 4,568,354, and 4,599,088 (Davis) describe stabilizing and
25 clarifying hazy, water-containing fuels that include about 0.10-0.50 wt % water by adding surfactants.

U.S. Patent No. 4,395,266 (Han) describes a stabilized, water-in-mineral oil emulsion
including 1-50% by volume water, in which the average particle size of the water droplets is 0.1-
25 microns.

30 U.S. Patent No. 4,083,698 (Wenzel) describes a water-in-oil emulsion of a hydrocarbon fuel, water, a water-soluble alcohol, and a combination of various surfactants. Wenzel teaches that the percentage of water by weight in the composition should range from about 0.1-10%, and

reports that clear compositions that are stable against phase separation over a wide range of temperatures result.

U.S. Patent No. 4,048,963 (Cottell) describes production of a water-in-oil emulsion including 10-50% water via sonic agitation in a continuous process just upstream of a combustion chamber. Very fine water droplets are reportedly produced, and it is reported that the flame temperature of combustion in internal combustion engines using the mixture is decreased while the total amount of power produced by the engine is as great as that produced by burning a comparable amount of unemulsified fuel.

While the above and other reports represent useful developments in the area of oil-water mixtures, a need exists in the art for improved, clean-burning, efficient, high-energy producing fuels producible on a commercially-viable scale. It is, therefore, an object of the invention to provide a water-fuel mixture having a high concentration of water, a low concentration of emulsifier (surfactant) that is efficient, low in emissions, inexpensive to produce, and thermally stable over a long period of time.

Summary of the Invention

The present invention involves, according to one aspect, the recognition that water-in-oil emulsions, as opposed to oil-in-water emulsions, and in particular water-in-oil emulsions having extremely small aggregates exhibit improved characteristics as fuels combustible in internal combustion engines and the like. It has been found that such fuels can be produced using components which minimize emission of certain toxic pollutants by careful selection and tailoring of components other than water and oil, and can be produced at commercially-viable expense. The discoveries of the invention allow production of a variety of aqueous/nonaqueous mixtures not limited to mixtures of water and fuel.

In one aspect, the invention is a composition that is an emulsion of an aggregate component partitioned into a plurality of discontinuous aqueous aggregates in a continuous nonaqueous component phase. The aqueous aggregates together have an average cross-sectional dimension of not more than about 100 nm. The emulsion has an aqueous content of at least about 8 wt %.

In another embodiment, a composition of the invention includes a mixture of an aqueous phase and a nonaqueous phase including at least about 8 wt % aqueous component. The mixture has a phase boundary area between aqueous and nonaqueous phases of at least about 5 m²/g

aqueous phase.

In some embodiments, the aqueous component is water and the nonaqueous component is fuel, and a surfactant that is free of certain toxic pollutant precursors, for example a surfactant free of nitrogen, is used. The water phase of fuel mixtures of the invention can form micelles
5 having average cross-sectional dimensions, or average dynamic diameters, that are very small. High water contents, and high phase boundary areas are achievable.

In another aspect, the invention provides a kit. The kit includes surfactant molecules that each have a polar section and a non-polar section. The surfactant molecules are constructed such that when they are mixed with a composition including a set ratio of an aqueous component and
10 a nonaqueous component they will form an aqueous-in-nonaqueous emulsion that includes aqueous aggregates of a first cross-sectional dimension in the nonaqueous component, and the surfactant molecules arranged at interfaces between the aqueous aggregates and a nonaqueous phase defined by the nonaqueous component, with the non-polar sections of the surfactant are oriented away from the aqueous micelles into the nonaqueous phase. The kit also includes co-
15 surfactant molecules that each include a polar section less hydrophilic than the polar section of the surfactant molecules, and a non-polar section. The co-surfactant molecules are constructed such that, when mixed with the surfactant and the composition, the co-surfactant molecules are able to insert between the non-polar sections of the surfactant molecules to form micelles of a second cross-sectional dimension less than the first cross-sectional dimension. The kit can
20 include the surfactant molecules and co-surfactant molecules mixed together, mixed together as a part of an overall composition including other species, packaged together but separately, packaged together and separately with other components, and the like. The surfactant/co-surfactant kit can be used as a surfactant system in an aqueous/nonaqueous emulsion of the invention.

25 According to another aspect, the invention provides a method of combustion. The method involves igniting fuel in the presence of water under conditions in which the water participates in a fuel reforming reaction. Products of the fuel reforming reaction then are combusted. According to one embodiment, the fuel is ignited in the presence of water and a catalyst that catalyzes the fuel reforming reaction. The catalyst can be a surface of an internal
30 combustion engine.

According to another aspect, the invention provides a method involving combusting fuel under set conditions in the presence of water at a temperature lower than that at which the fuel

would combust under the set conditions in the absence of water. The method is carried out by creating radical species at the surface of a catalyst that participate in the combusting step.

In another aspect, the invention provides a method of making an aqueous-in-nonaqueous emulsion. The method involves providing a nonaqueous component and adding a surfactant system to the nonaqueous component to form a mixture. Subsequently, an aqueous component and a stabilizer are alternately added to the mixture. That is, following formation of the mixture, first an aqueous component is added, then stabilizer, then aqueous component again, or after formation of the mixture first stabilizer is added, then aqueous component, then stabilizer.

Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures is represented by a single numeral. For purposes of clarity, not every component is labeled in every figure.

Brief Description of the Drawings

Fig. 1 is a schematic illustration of a portion of a micelle of a water-in-oil emulsion having a relatively large diameter;

Fig. 2 is a schematic illustration of a portion of a micelle of a water-in-oil emulsion having a small diameter relative to the micelle of Fig. 1;

Fig. 3 is a schematic illustration of a portion of a reduced-size aqueous-in-nonaqueous micelle including surfactant molecules having non-polar sections between which are inserted co-surfactant molecules; and

Fig. 4 is a schematic illustration of a stabilizing surfactant of the invention including polar portions that interact in a stabilizing manner with water.

Detailed Description of the Invention

The present invention provides two-phase, aqueous/nonaqueous systems having improved properties. The systems can find use in any of a wide variety of applications as described above and, in a particularly preferred embodiment, the invention provides water-in-oil emulsions useful as combustible fuels. While fuel emulsions are described hereinafter, it is to be understood that the disclosure herein of exemplary components and combinations of components

for use in the invention, and selection criteria and screening techniques for formulating emulsions of the invention, are applicable to any useful aqueous-in-nonaqueous emulsion. In that light, components such as surfactants are described below and described in documents incorporated by reference herein that may not be suitable for clean-burning fuel mixtures, but would be suitable for many other emulsions. Guidance is provided below in selection of components that would be most suitable for clean-burning fuels.

The aqueous/nonaqueous mixture of the invention is preferably an isotropic micellar phase of the "reversed" type, that is, micelles surrounded by surfactant molecules arranged with polar sections pointing toward the micelle and non-polar sections facing outward. As used herein "micelle" means an isolated aqueous aggregate having any shape, for example cylindrical, spherical, ellipsoidal, irregular shapes, etc. Generally, in emulsions of the invention, the aqueous aggregates will form spherical micelles.

The aqueous and nonaqueous components are preferably liquids at room temperature, but need not be. One component of the two components, or both components, can be solid enough at room temperature to be self-supporting. A cosmetic micellar formulation including a nonaqueous component that is soft but solid at room temperature, in which aqueous aggregates are contained, the overall composition being in the form of a cream at room temperature, is one example of aqueous-in-nonaqueous emulsions encompassed by the invention.

In preferred fuel embodiments of the invention, the arrangement has high combustibility, which can be achieved by selection of surfactant systems that themselves are combustible, as described below.

The micelle systems preferably have high thermal and temporal stability, that is, they are storable over extended periods of time at temperatures that do not require extreme care in storage.

Compositions of the invention are, according to preferred embodiments, stable for at least about 20 microseconds within a temperature range of from about 0.5°C to about 45°C, more preferably for about 1 minute, more preferably for about 1 hour, more preferably still for about one day, more preferably still for about one month, and more preferably still for about one year within this temperature range of from about -5°C to about 45°C. According to another aspect, the composition is preferably stable for at least about one minute within a temperature from about -10°C to about 50°C, more preferably within a range from about -20°C to about 60°C. In one preferred embodiment the emulsion is stable for at least about 10 microseconds and a

temperature of at least about 2000°C.

The emulsions of the invention include discontinuous aqueous aggregates in a continuous nonaqueous phase. This means that separate, isolated regions of aggregates of an aqueous component are contained within a continuous nonaqueous phase defined by a nonaqueous component. The discontinuous aqueous aggregates in the nonaqueous phase typically take the form of micelles having an average cross-sectional dimension of not more than about 100 nm. In another aspect, the micelles preferably have an average dynamic diameter of not more than about 100 nm. "Average dynamic diameter" is meant to define micelle diameters in which the micelles are relatively set in shape, or the average diameters of micelles which are fluid and are constantly changing in shape. Where micelles are fluid and constantly changing in shape, the average dynamic diameter is the average diameter of the micelle in a state in which it is essentially spherical. Average cross-sectional dimensions or average dynamic diameters of micelles of the invention preferably are not more than about 50 nm, more preferably not more than about 25 nm, more preferably not more than about 15 nm, more preferably not more than about 10 nm, and most preferably not more than about 5 nm, although micelles smaller than 5 nm and even 3 nm are effective.

According to another aspect of the invention the composition is a mixture of an aqueous phase and a nonaqueous phase, the mixture including a phase boundary area between the aqueous and nonaqueous phases of at least about 5 m²/g aqueous phase. This mixture can take the form of an emulsion including a discontinuous aqueous phase component, for example micelles, in a continuous nonaqueous phase, and the aqueous phase is present in an amount of at least about 8 wt %. Preferably, the phase boundary area is at least about 10 m²/g aqueous phase, more preferably at least about 15 m²/g, more preferably at least about 20 m²/g, more preferably at least about 25 m²/g, more preferably at least about 50 m²/g, more preferably still at least about 70 m²/g, and most preferably at least about 90 m²/g of the mixture. In each of the above-described aspects, namely the aqueous-in-nonaqueous emulsion and the aqueous phase/nonaqueous phase mixture, the aqueous phase is present in an amount preferably of at least about 12 wt %, more preferably at least about 15 wt %, more preferably at least about 20 wt %, more preferably at least about 25 wt %, more preferably at least about 30 wt %, which has been found to be optimum in some embodiments. In other embodiments the aqueous phase is present in an amount of at least about 40 wt % may be advantageous, and in others at least about 50 wt % based on the weight of the emulsion or mixture.

The aqueous/nonaqueous mixture or emulsion of the invention preferably has an electrical conductivity essentially equal to that of the nonaqueous phase. This is because the aqueous phase, which could be conductive, is in the form of isolated regions, and the only continuous phase is nonaqueous and non-electrically conductive. The composition, according to preferred embodiments, has an electrical conductivity no more than about 450 microsiemens, the approximate electrical conductivity of tap water. According to a more preferred embodiment, the composition has an electrical conductivity of no more than about 20 microsiemens. Where the mixture or emulsion involves a continuous diesel fuel component, the composition will have a conductivity of about 2-4 microsiemens, which is the approximate conductivity of diesel fuel.

When used as a fuel, compositions of the invention preferably are not acidic since acidity generally causes corrosion in engines. Accordingly, the aqueous phase of compositions of the invention preferably has a pH of greater than about 3, more preferably greater than about 5, and more preferably greater than about 6. The composition as a whole preferably has a pH of greater than about 3, more preferably greater than about 5, and more preferably greater than about 6, as well. The aqueous phase of compositions of the invention preferably has a purity level of at least about 95%.

The invention provides compositions that are aqueous/nonaqueous mixtures having good viscosity values according to preferred embodiments. Viscosity of aqueous-in-nonaqueous emulsions typically increases as the size of isolated phase regions, or micelle, increases.

Compositions of the invention include isolated phases of average dynamic diameter, or average cross-sectional dimension low enough that viscosity is low. In particular, compositions of the invention have a viscosity of less than about 50 centipoise at 25° C according to preferred embodiments. More preferably, compositions of the invention have a viscosity of less than about 40, more preferably less than about 30, more preferably less than about 20, more preferably still less than about 15 centipoise at 25° C, and most preferably less than 10 centipoise at 25°C.

As used herein, "nonaqueous" is meant to define material such as a fluid that is immiscible with water. That is, a liquid that when mixed with water will form a two-phase mixture. The non-aqueous phase need not be liquid, but can be a solid or semi-solid lipid or other nonpolar substance that is not soluble in water. For example, oils such as coconut oil and other hydrocarbons used in cosmetics, moisturizers, and the like are included. Additionally, corn oil, cottonseed oil, soya, fish oil, lanolin, and the like can define the non-aqueous phase. In the preferred embodiment, the non-aqueous phase is a combustible, carbonaceous fuel such as

gasoline, kerosene, diesel fuel, aviation fuel such as jet fuel, and in some cases petroleum, especially petroleum that is of relatively low molecular weight in its crude form, and the like. "Fuels" is meant to define substances which are combustible in the presence of oxygen and heat to produce energy. Additional fuels include ligroin, mineral spirits, petroleum ether, turpentine, nitrobenzene, nitroethane, nitromethane, 1-nitropropane, and the like (although fuels that contain very low levels of nitrogen, sulfur, and phosphorous are particularly preferred since combustion of such fuels generally leads to unacceptable levels of toxic emissions). Fuels of the invention can include, in general, any products of petroleum distillation that are immiscible with water. The nonaqueous phase can include a mixture of any of a plurality of nonaqueous components, such as are typically found in commercial fuels.

The aqueous phase can be any liquid miscible with water, that is, any liquid that, when admixed with water, can form a room-temperature, single-phase solution. The aqueous phase, if solid at the temperature being tested, will interact with water to form a water contact angle of less than about 80°. Preferably, the aqueous phase is water at a purity level of at least about 95%, or preferably at least about 98%, and more preferably still water at a purity level of at least about 99.5%.

As used herein, "surfactant" defines a molecule that, when combined with an aqueous component and a nonaqueous component, will facilitate assembly of separate aqueous and nonaqueous phases. Surfactants of the invention can be selected from any of a wide variety of known surface-active species in accordance with selection criteria below. Surfactants which can be selected includes those in U.S. Patent Nos. 4,083,698 and 4,821,757, both incorporated herein by reference, as well as commonly-owned, co-pending U.S. application serial no. 08/500,710, filed July 11, 1995 by Ahern, et al., entitled "Combustion of Nanopartitioned Fuel", incorporated herein by reference. In particular, a wide variety of classes of surfactants including but not limited to alkyl sulfates and quaternaries, including heterogeneous polyoxyethylenes, glucamides, digitonin, bile acids, sulfo betaines, betaines, alkyldimethylamine oxides, alkyl glucosides, alkyl maltosides, lecithins and lysolecithins, homogeneous polyoxyethylenes, and alkyl thioglucosides. Specifically, polyethylene glycol dodecyl ether, octanoyl-N-methylglucamide, nonanoyl-N-methylglucamide, decanoyl-N-methylglucamide, nonyl glucoside, nonaethylene glycol octylphenyl ether, octyl glucoside, octyl thioglucoside, polyethylene polypropylene glycol, monosodium taurocholic acid, sodium taurodesoxycholate, nonaethylene glycol mono-dodecyl ether, nonaethylene glycol octylphenol ether, nonaethylene

glycol octylcyclohexyl ether, heptaethylene glycol octylphenyl ether, heptaethylene glycol octylcyclohexyl ether, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monooleate, n-octylsulfobetaine, n-decylsulfobetaine, n-dodecylsulfobetaine, n-tetradecylsulfobetaine, n-hexadecylsulfobetaine, N,N-bis(3-D-
5 gluconamidopropyl) cholamide, polyoxyethylene lauryl ether, octaethylene glycol monododecyl ether, nonaethylene glycol monododecyl ether, cetrinmonium bromide, 3-[(3-cholamidopropyl) dimethylammonio]-1-propanesulfonate, 3-[(3-cholamidopropyl) dimethylammonio]-2-hydroxypropane-1-sulfonate, cholic acid (monosodium salt), decyl glucoside, decyl maltoside, N,N-bis (3-D-gluconamidopropyl)deoxycholamide, deoxycholic acid
10 (sodium salt), digitin, dodecyl maltoside, N-Dodecyl-N,N-dimethylglycine, dioctyl sodium sulfosuccinate, lauryldimethylamine oxide, decaoxyethylene monolauryl ether, octaethylene glycol isotridecyl ether, polyoxyethylene isotridecyl ether, glycocholic acid (sodium salt), glycodeoxycholic acid (sodium salt), heptyl glucoside, hexyl glucoside, heptyl thioglucoside, N,N-Dimethyl-N-dodecylamine oxide, sodium lauryl sulfate, and equivalent surfactants may be
15 selected. Particularly preferred classes include polyglycerol-derived esters and ethers, polyethoxylated-derived esters and ethers, polysubstituted amines, aryl and alkyl ethylene oxide adducts, and phenolic ethylene adducts.

For fuels, surfactants that are most preferred do not include nitrogen, sulfur, phosphorous, or acids as these species can raise pollutant levels and/or cause corrosion of engines.

20 Additionally, most preferred surfactants for fuels are low in C-O, C-OH, and C-O-C bonds, which are less-readily combustible than some other species. Accordingly, for fuels it is preferred that these species be minimized.

Criteria in accordance with the invention that can be used to select suitable aqueous phases, nonaqueous phases, and surfactants suitable for use in the invention include, first, a
25 simple screening test to determine whether an aqueous-in-nonaqueous emulsion has been created. First, if water-soluble, lipid-insoluble ink is added to an emulsion, if the emulsion is an aqueous-in-nonaqueous emulsion the ink will form a separate phase, since it is not miscible with the continuous, nonaqueous phase, but in the case of a nonaqueous-in-aqueous emulsion the ink will dissolve in the continuous, aqueous phase giving the appearance of dissolution of the ink in
30 the entire mixture. In a second screening test the aqueous phase can be made slightly electrically conductive and, if the emulsion is slightly electrically conductive, then the continuous phase is aqueous, i.e. a nonaqueous-in-aqueous phase results. If the mixture is not electrically

conductive, then an aqueous-in-nonaqueous emulsion results. As a third screening step, if the mixture is optically clear, then very small aqueous aggregates in a nonaqueous, continuous phase has been formed. For example, preferred cross-sectional dimensions and preferred dynamic diameters of emulsions of the invention will exhibit optical clarity.

5 Predictive criteria for surfactant system selection now will be discussed. As used herein, "surfactant system" defines one or more types of molecules that, when combined with an aqueous component and a nonaqueous component, will facilitate assembly of separate aqueous and nonaqueous phases. In one selection technique, a relationship between the balance of hydrophilic and lipophilic portions of a surfactant is matched with the probability, in an overall
10 aqueous component/nonaqueous component mixture, of having a polar group as a nearest neighbor. The relationship is expressed as Equation 1

$$HLB \text{ required} = \frac{\text{probability of having polar group as nearest neighbor}}{5} \quad (1)$$

where HLB is the approximate minimum hydrophilic/lipophilic balance required in the surfactant. The minimum approximate HLB of the surfactant is matched with the polar neighbor
15 probability of the mixture. The probability of having a polar group as nearest neighbor in the overall aqueous component/nonaqueous component mixture can be determined by one of ordinary skill in the art via a Monte Carlo simulation. The approximate HLB required also can be approximated as follows, especially in the case of a mixture having approximately 30% or less water. The HLB required according to this method is approximately equal to the molecule
20 volume fraction of water times the energy involved in a bond between a water molecule and a surfactant molecule, considering interactions including hydrogen bonding and Van der Waals interactions, and assuming that the volume of a CH₂ group of a hydrocarbon chain is equal to the volume of a water molecule.

It can be advantageous also to approximately match the chain length of the non-polar
25 portion of the surfactant with the average chain length of the nonaqueous component of the mixture.

The system works as follows. For isooctane, for example, with 20 wt % water, the probability of having a polar group as the nearest neighbor is 41, therefore the approximate HLB required should be at least 8.26. With 30 wt % water in isooctane the probability is 61, therefore

the approximate HLB required is 12.25. For 50 wt % water, the probability is 81, therefore the approximate HLB required is 16.21. If, for example, an ethylene oxide surfactant is being tailored for use with an isooctane/water system, one would select a main hydrocarbon chain that is good for interaction with isooctane, for example a chain length of C5 (pentyl). It is to be understood that chain length means degree of CH₂ group present, for example in a branched chain; it is not to be implied that a linear chain need be used, or that a dimension of the molecule is defined by chain length. To determine the desired number of ethylene oxide units, at 30 wt % water in isooctane, the HLB required should be at least 12.25, therefore the mol % of ethylene oxide units is $12.25 \times 5 = 61\%$. C₅H₁₂:72 g/gmol yields 39%. EO:45 g/gmol yields 61%.

Therefore, three moles of ethylene oxide per mol of pentanol are used.

This system can be aided by addition of a co-surfactant which can minimize micelle size. A goal is illustrated schematically in Figs. 1 and 2. Fig. 1 illustrates a portion of an aqueous-in-nonaqueous micelle 10 including an aqueous phase 12 separated from a nonaqueous, continuous phase 14 by a partition 16 defined by an aggregation of individual surfactant molecules 18.

Surfactant molecules 18 include polar portions 20 that face and/or integrate with aqueous phase 12 and non-polar portions 22 that face and/or integrate with nonaqueous phase 14. Fig. 2 is a schematic illustration of an arrangement similar to that of Fig. 1 but in which a smaller micelle 24 is formed. To form a smaller micelle 24 of the same components as those that define the emulsion with larger micelles 10, surfactant molecules must promote smaller micelle formation. Toward that end, surfactant molecules 26 should include smaller polar sections 20, or larger non-polar sections 25, or both, or non-polar sections 25 that are sterically bulkier than non-polar sections 22 of surfactant molecules 18, to encourage spreading of the non-polar sections. This arrangement has its limits, however, and therefore according to one embodiment of the invention a co-surfactant is added that aids in creating smaller micelles by creating spacing between hydrophobic portions of surfactants increasing the radius of curvature achievable with a micelle.

Referring now to Fig. 3, an aqueous-in-nonaqueous emulsion 28 is illustrated including an aqueous phase 30, a nonaqueous phase 32, and surfactant molecules 34 separating the phases. The system includes a co-surfactant molecule 36 having a polar portion 38 and a non-polar portion 40. The polar portion 38 of co-surfactant molecule 36 is smaller than the polar portion 33 of surfactant molecule 34 and the non-polar portion 40 of the co-surfactant molecule 36 is smaller than the non-polar portion 35 of surfactant molecule 34. Polar portion 38 of co-surfactant molecule 36 also may be selected to be slightly less polar than polar portion 33 of

surfactant molecule 34. In this way, co-surfactant molecules 36 will insert to a greater degree between non-polar portions 35 of surfactant molecules 34 and aid in spreading, rather than inserting between polar portions 33 of surfactant molecules 34. Those of ordinary skill in the art can select surfactant molecules suitable for use as co-surfactant molecules 36 based upon these teachings. An additional, relatively non-polar co-surfactant molecule 42 is provided which inserts between non-polar portions 35 of surfactant molecules 34. The relatively non-polar co-surfactant molecules 42 are slightly more polar than the non-polar components that make up nonaqueous phase 32. Therefore, co-surfactant molecules 42 are not dissolved within nonaqueous phase 32 but are attracted by the polar nature of aqueous aggregate 30 and polar portions 33 and 38 of surfactant molecules 34 and 36, respectively. Co-surfactant molecules 42 are also non-polar to the extent that they are attracted to non-polar portions 35 of surfactant molecules 34. Examples of suitable co-surfactant molecules 42 include hydrocarbons of from about C2 to about C20 in size containing sufficient polar heteroatoms or side groups, for example ketone functionalities, to result in chemical attraction sufficient to cause molecules 42 to be retained in the vicinity of aqueous aggregates 30, between non-polar portions 35 of surfactant molecules 34. As used herein "chemical attraction", or "chemically attracted" means bonding such as hydrogen bonding, Van der Waals interaction and the like that causes molecules to remain together rather than integrating into or dissolving within the aqueous component 30 or nonaqueous component 32. This attraction leads to binding. As used herein "bind" is meant to define interaction between two molecules in a manner defined by chemical attraction, about.

In a particularly preferred embodiment, co-surfactant molecules 36 are stabilizers of the micelle arrangement. "Stabilizer" is meant to define a co-surfactant molecule that, when mixed with a surfactant molecule, will interact with its hydrophilic head group with the arrangement of hydrophilic head groups 33 of surfactant molecules 34 in a manner interfering with any ordered assembly of head groups 33 in a manner that would improve flexibility of the surface of the micelle. The head groups 38 of co-surfactant molecules 36 that are stabilizers interfere with ordered arrangement of head groups 33 of surfactant 34 thereby imparting flexibility to the surface of the aqueous aggregate 30 and stabilizing the system. A preferred class of stabilizers are alcohols ROH, where R is an alkyl chain of from about C2 to about C10 in length. The stabilizer is less polar than the surfactant 35.

The non-polar section of surfactant molecules of the invention typically comprises a hydrocarbon chain at least C2 in length. Preferably, the hydrocarbon chain of the non-polar

section is at least C4 in length, more preferably at least C6 in length, and more preferably still at least C8 in length.

Another embodiment of the invention is a method of making an aqueous-in-nonaqueous emulsion. The method involves providing a nonaqueous component, and adding a surfactant system to the nonaqueous component to form a mixture. Then, an aqueous component and stabilizer are alternately added to the mixture. That is, the aqueous component is added, then stabilizer, then aqueous component, or stabilizer is added, then aqueous component, and then stabilizer. The aqueous component and stabilizer are alternately added until the emulsion is of proper component ratio. Adding aqueous component and stabilizer alternately prevents the composition from falling into metastable wells by preventing over-concentration of either the aqueous component or stabilizer that could lead to phase separation or gelation. The aqueous component and stabilizer are added, alternately, preferably in amounts less than about 30% of their total final concentration, more preferably less than about 15% of their total final concentration.

Equation 1, above, and its related discussion can be used to select a combination of surfactant molecules 34 and co-surfactant molecules 36 and/or 42 useful in forming very small micelles. One uses equation 1 to determine the approximate HLB required of the surfactant/co-surfactant system as described above for selection of a surfactant. Then, one matches this HLB with HLB_i , as defined in Equation 2.

$$HLB_i = \frac{\text{mol fraction (\%)} \text{ of polar groups}}{5} \quad (2)$$

For example, in a system including 80 wt % $C_6(EO)_3$ (where $C = CH_2$ and $EO = CH_2CH_2O$, optionally terminating in OH) and 20 wt % of co-surfactant molecules having 10% polar groups, the following relationship would exist. In C_6EO_3 , 50% carbons are of polar nature and 50% carbons are of non-polar nature. Therefore, the HLB_i is 50%/5, that is, 10. For the co-surfactant system, the HLB_i is 10%/5, or 2. Therefore, the HLB of the surfactant system is 0.80 (10) plus 0.2 (2), or 8.4. One would match approximately this HLB of the surfactant system with the approximate HLB required of Equation 1.

The selectability and predictability of surfactant systems for use in the invention allows

use of less wt% surfactant per weight composition or, in another aspect, less surfactant per aqueous content. Preferably, the surfactant is present in the emulsion in an amount not more than about 40 wt % based on the weight of the composition, more preferably not more than about 30 wt %, more preferably not more than about 20 wt %, more preferably not more than about 10 wt % and most preferably not more than about 5 wt % based on the weight of the composition. In another aspect, the emulsion has an aqueous content of at least 20 wt % and includes surfactant in an amount of not more than 10 wt %. Preferably, the emulsion has an aqueous content of at least 30 wt % and includes surfactant in an amount not more than about 15 wt %. More preferably still, the emulsion has an aqueous content of at least 40 wt % and includes surfactant in an amount not more than about 20 wt %.

One class of preferred surfactant molecules have polar sections that can "wrap" about water molecules, that is, polar portions which have the length and flexibility to interweave with water molecules. This arrangement is illustrated in Fig. 4 in which an aqueous-in-nonaqueous micelle 44 is made up of water molecules 46, nonaqueous phase 48, and surfactant molecules 50. The surfactant molecules each include a non-polar portion 52 that interacts with nonaqueous phase 48 and a polar portion 54 having the length, polarity, and flexibility to interweave with water molecules 46. Polar portions 54 of surfactant molecules 50 preferably are created from species that can hydrogen bond with water, and can rotate about single bonds (preferably free of multiple bonds) for flexibility, for example ethylene oxide units. In particular, polyethoxylated alcohols such as those of the formula $(CH_2)_x(EO)_y$, where X and Y are each about 2 to about 12 are preferred which can be synthesized by those of ordinary skill in the art using alcohol, an epoxide, and a catalyst that can be of alkaline or acid character. Examples of alkaline catalysts are sodium hydroxide, potassium hydroxide, and magnesium oxide.

One set of preferred surfactant, co-surfactant, emulsion arrangements include those listed in Table 1 below.

Ethylene oxide surfactants offer the advantage of flexible polarity through the manipulation of the number of ethylene oxide units, flexible hydrophobicity through the manipulation of carbon tail chain length, and flexible hydrophilicity through terminal group selection, and the ability to interweave with water molecules. Polyglycerides offer the advantage that particle sizes are particularly small when using the surfactants. Polyethoxylated carboxylic acid surfactants increase overall polarity, and reduce chain length. The use of linear alcohols also is avoided, and high water solubilization is achieved. Viscosity is reduced. Additionally,

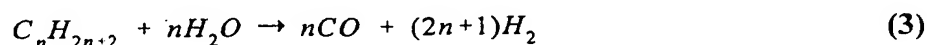
with these surfactants ethylene oxide wrapping, or interweaving with water is achieved. Polyethoxylated amines do not require the need for co-surfactants and decreased head group volume is achieved. Particles of less than 10 nm are created with these species.

According to a particularly preferred embodiment, a surfactant that has a polar section
5 and a non-polar section in which the polar section includes at least two hydrophilic chains of at least C2 in length that are joined to a non-polar hydrocarbon chain via linkage that is free of N, S, and P, are provided. For example, double-chain ethoxylated alcohols can be used which reduce need for co-surfactants by decreasing head group volume with increased polarity and decrease the need for hydrophobic character. Functionality is similar to polyethoxylated amines, although
10 no nitrogen is present, reducing emissions in combustion of fuels. As used herein, "hydrocarbon" is meant to include alkyl, alkenyl, alkynyl, cycloalkyl, aryl, alkaryl, aralkyl, and the like, optionally interrupted by hetero groups that can include -O-, -CONH-, -CONHCO-, -NH-, -CSNH-, -CO-, -CS-, -S-, -SO-, $-(OCH_2CH_2)_nR$ (where $n=1-10$), $-(CF_2)_n-$ (where $n = 1-10$), olefins, and the like.

One advantage provided by the aqueous component of the fuel mixture of the invention is
15 that, by introducing water in the combustion chamber, the temperatures during the cycle are effectively reduced, typically on the order of 200° C. Under lower temperature conditions, the expansion coefficient γ , calculated as the ratio of the heat capacity at constant pressure, C_p , divided by the heat capacity at constant volume, C_v , effectively increases. In "Internal
20 Combustion Engine Fundamentals", Heywood, J.B., 1988 McGraw-Hill, pp. 170, the relation between γ and the efficiency through which an engine transforms heat emitted from the combustion into useful work, thermal efficiency, is depicted. By decreasing the temperature of the combustion chamber from 1800 °C to 1600 °C, the value of γ is increased from 1.25, typical value for diesel engines, to 1.4. At a compression ratio of 20, typical for a diesel engine,
25 the thermal efficiency is increased from 50 to 65% accounting for an effective 30% increase in overall fuel efficiency. The reason why γ increases rises from the fact that both C_p and C_v decrease with decreasing temperature, however, for gaseous species the change in C_p is small relative to the change in C_v , and therefore their quotient increases.

It has been found in accordance with the invention that particularly small aqueous
30 aggregates in the fuel mixture are particularly advantageous. While not wishing to be bound by any theory, it is believed that the aqueous-in-nonaqueous emulsions of the invention form particularly efficient combustible fuel mixtures due to their participation in a water reforming

reaction. The reaction requires a catalyst which can be a metallic surface such as a surface of an internal combustion engine, or an added catalyst. A catalyst such as Si, Al, a transition metal, a rare earth compound, a noble metal, or any oxide, nitride, or carbide of these can be used. In a preferred embodiment in which fuels are burned in an internal combustion engine, the catalyst
 5 can be a surface of the combustion chamber of the internal combustion engine. The reaction scheme proceeds as in Equations 3-5, below which equations are intended to represent chemistry taking place in the presence of the catalysts.

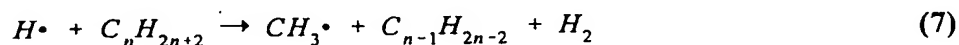
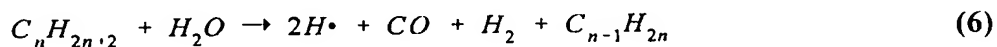


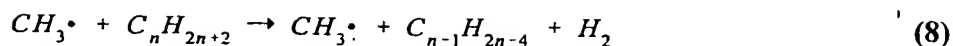
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15 In the reaction, a time-consuming process in which a plurality of steps each removing one CH₂ unit of an alkane is avoided. This is due to the fact that a reaction scheme as in Equations 6-10, below, takes place between Equations 3 and 4 above. This reaction scheme results in the production of small, low-molecular weight hydrocarbons rapidly, increasing combustion efficiency and adding to the energy obtainable from the combustion of fuel.

20





Additionally, as fuel begins to burn from the outside some hydrocarbons do not come in contact with sufficient oxygen to fully ignite and burn, therefore they char, producing
 10 particulates called soot. The presence of water as small aggregates within the hydrocarbon matrix helps avoid soot production. The bursting of these aggregates at high temperatures produce a disruption in the oil continuous phase, effectively increasing the fuel/air contact surface, allowing for a full combustion. Aqueous aggregates less than about 20 nm in dimension allow for bursting.

15 The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not exemplify the full scope of the invention.

In the following examples, characterization of emulsions was made using dynamic laser
 20 light-scattering techniques.

Example 1: Formulation of Stable, Aqueous-in-Nonaqueous Emulsion

A clear, stable, fuel-water nanoemulsion was prepared by
 mixing 80 wt % of a polyethoxylated alcohol with 20 wt % of polyglyceryl-4-monooleate at 15°
 25 C and 60 RPM for 20 minutes. The alcohol had the formula $R(OCH_2CH_2)_6OH$, where R is a C8 paraffinic chain. 18 grams of this mixture were added slowly while stirring to 50 grams of low-

sulfur diesel fuel (average carbon chain length of 16) at the same temperature.

50 grams of purified deionized water were added to the mixture of diesel fuel and surfactants. The mixture turned milky white under vigorous agitation. A mixture consisting of 40 wt % 1- butanol and 60% 1-hexanol was obtained by stirring. 5 grams of this mixture were slowly added while stirring to the previous preparation containing diesel, water, and surfactants. The resulting mixture was a clear, oily liquid. The final composition of the mixture was:

Deionized Water	40.65 wt %
Diesel Fuel	40.65 wt %
10 1-butanol	1.62 wt %
1-hexanol	2.43 wt %
polyethoxylated octanol	11.7 wt %
polyglycerol-4-monooleate	2.95 wt %

15 The mixture showed a viscosity of 12.13 cP, a density of 0.87 g/cc, and micellar average diameter of 7.5 nm at 15° C.

Examples 2-7: Formulation of Water-in-Fuel Emulsions

Fuel mixtures were prepared in the fashion described in Example 1, using the following hydrocarbon mixtures instead of diesel: gasoline (C6-C10), kerosene (C10-C14), light diesel (C14-C18), heavy diesel (C12-C24), gasoil, and heating oil (> C24). All formed stable water-in-fuel nanoemulsions.

Examples 8-13: Preparation of Water-in-Fuel Emulsions Using Tap Water

25 Fuel mixtures were prepared as in Examples 2-7, using tap water rather than deionized water. Stable nanoemulsions resulted.

Examples 14-17: Preparation of Water-in-Fuel Emulsions

Emulsions were prepared as in Example 1, using the systems as in Table 1.

Surfactant	Cosurfactants	Range of Water Contents	Range of HLB	Range of Particle Sizes
Polyethoxylated alcohol:C8EO6	Polyglyceryl Oleates; Linear Alcohols	5-55%	7-14.5	140-2.5 nm
Polyethoxylated alcohols:Mixture C9-C11	Polyglyceryl Oleates; Linear Alcohols	5-55%	6-12.5	200-5 nm
Ethoxylated Phenols: C6-C8-EO6	Polystearates and Alcohols	5-50%	4-10	25 μ m-30 nm
Polyethoxylated Alcohols:Mixture C9-C11	POE Sorbitan, alcohols.	10-40%	8-11	100-5 nm

Table 1Further Examples

Fuel mixtures were prepared as described above with fuel:water ratios (wt %) of from 1:1 to 6.5:1. Diesel fuel was used.

Combustion Testing of Nanostructured Fuels

Many of the above-described exemplary water-in-oil fuel emulsions were tested using an unmodified, 4-cycle diesel engine. Tests were conducted with nanostructured aqueous fuels in comparison with similar fuels without aqueous component. Particulate emissions was reduced in all cases, with typically up to about or within the range of from about 85-90% reduction in particulate emissions.

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that actual parameters will depend upon the specific application for which the methods and apparatus of the present invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described.

CLAIMS

1. A composition comprising:

an emulsion of discontinuous aqueous aggregates in a continuous nonaqueous phase, the
5 discontinuous aqueous aggregates including separate, isolated portions having an average cross-sectional dimension of not more than about 100 nm and the emulsion having an aqueous content of at least about 8 wt %.

2. A composition as in claim 1, the mixture including a phase boundary area between aqueous
10 aggregates and the nonaqueous phase of at least about 5 m²/g aqueous phase.

3. A composition as in claim 1, the mixture including an interface area between aqueous and nonaqueous phases of at least about 15 m²/g aqueous phase.

15 4. A composition as in claim 1, the mixture including an interface area between aqueous and nonaqueous phases of at least about 25 m²/g aqueous phase.

5. A composition as in claim 1, the mixture including an interface area between aqueous and nonaqueous phases of at least about 50 m²/g aqueous phase.

20

6. A composition as in claim 1, wherein the discontinuous aqueous aggregates comprises a plurality of micelles.

7. A composition as in claim 1, the emulsion including a surfactant molecule having a polar
25 section and a non-polar section, the non-polar section comprising at least one lipophilic hydrocarbon chain, the polar section comprising at least two hydrophilic chains each at least C2 in length, the at least two hydrophilic chains joined to the at least one hydrocarbon chain.

8. A composition as in claim 7, wherein the at least two hydrophilic chains of the surfactant
30 molecule are joined to the at least one hydrocarbon chain via linkage that is free of N, P, and S.

9. A composition as in claim 7, wherein the at least one lipophilic hydrocarbon chain of the

surfactant is at least C3 in length.

10. A composition as in claim 7, wherein the at least one lipophilic hydrocarbon chain of the surfactant is at least C4 in length.

5

11. A composition as in claim 7, wherein the at least one lipophilic hydrocarbon chain of the surfactant is at least C6 in length.

10 12. A composition as in claim 7, wherein the at least one lipophilic hydrocarbon chain of the surfactant is at least C8 in length.

13. A composition as in claim 1, further comprising a surfactant molecule that is a multi-chain ethoxylated alcohol.

15 14. A composition as in claim 1, wherein the emulsion includes a surfactant system including surfactant molecules each including a polar section and a non-polar section, constructed such that when mixed with a composition including a set ratio of an aqueous component and a nonaqueous component they will form an aqueous-in-nonaqueous emulsion including aqueous aggregates of a first average cross-sectional dimension in a nonaqueous phase and the surfactant molecules
20 arranged at interfaces between the aqueous aggregates and the nonaqueous phase with the non-polar sections of the surfactant oriented away from the aqueous aggregates into the nonaqueous phase; and

co-surfactant molecules each including a polar section that is less hydrophilic than the polar section of the surfactant molecules and a non-polar section, constructed such that when
25 mixed with the surfactant molecules and the composition, the co-surfactant molecules are able to insert between the non-polar sections of the surfactant molecules to form aqueous aggregates of a second average cross-sectional dimension less than the first cross-sectional dimension.

15. A composition as in claim 1, wherein the discontinuous aqueous aggregates in the
30 continuous nonaqueous phase defines a plurality of micelles having an average cross-sectional dimension of not more than about 50 nm.

16. A composition as in claim 15, the micelles having an average cross-sectional dimension of not more than about 25 nm.

17. A composition as in claim 15, the micelles having an average cross-sectional dimension of
5 not more than about 15 nm.

18. A composition as in claim 15, the micelles having an average cross-sectional dimension of not more than about 10 nm.

10 19. A composition as in claim 15, the micelles having an average cross-sectional dimension of not more than about 5 nm.

20. A composition as in claim 15, the micelles having an average cross-sectional dimension of not more than about 3 nm.

15

21. A composition as in claim 1, wherein the discontinuous aqueous aggregates in the continuous nonaqueous phase defines a plurality of micelles having an average dynamic diameter of not more than about 50 nm.

20 22. A composition as in claim 21, the micelles having an average dynamic diameter of not more than about 25 nm.

23. A composition as in claim 21, the micelles having an average dynamic diameter of not more than about 15 nm.

25

24. A composition as in claim 21, the micelles having an average dynamic diameter of not more than about 10 nm.

25. A composition as in claim 21, the micelles having an average dynamic diameter of not more
30 than about 5 nm.

26. A composition as in claim 21, the micelles having an average dynamic diameter of not more

than about 3 nm.

27. A composition as in claim 1, wherein the emulsion has a viscosity of less than about 50 centipoise at 25° C.

5

28. A composition as in claim 1, wherein the emulsion has a viscosity of less than about 40 centipoise at 25° C.

10

29. A composition as in claim 1, wherein the emulsion has a viscosity of less than about 30 centipoise at 25° C.

30. A composition as in claim 1, wherein the emulsion has a viscosity of less than about 20 centipoise at 25° C.

15

31. A composition as in claim 1, wherein the emulsion has a viscosity of less than about 15 centipoise at 25° C.

32. A composition as in claim 1, wherein the emulsion has a viscosity of less than about 10 centipoise at 25° C.

20

33. A composition as in claim 1, wherein the micelles have an essentially spherical average shape.

34. A composition as in claim 1, the emulsion having an aqueous content of at least about 12 wt %.

25

35. A composition as in claim 1, the emulsion having an aqueous content of at least about 15 wt %.

36. A composition as in claim 1, the emulsion having an aqueous content of at least about 20 wt %.

30

37. A composition as in claim 1, the emulsion having an aqueous content of at least about 25 wt %.

38. A composition as in claim 1, the emulsion having an aqueous content of at least about 30 wt %.

39. A composition as in claim 1, the emulsion having an aqueous content of at least about 40 wt %.

40. A composition as in claim 1, the emulsion having an aqueous content of at least about 50 wt %.

41. A composition as in claim 1, wherein the composition has an electrical conductivity of no more than about 450 microsiemens.

42. A composition as in claim 1, wherein the composition has an electrical conductivity of more than about 20 microsiemens.

43. A composition as in claim 1, wherein the emulsion has an electrical conductivity essentially equal to that of the nonaqueous phase.

44. A composition as in claim 1, wherein the emulsion has a pH of greater than about 3.

45. A composition as in claim 1, wherein the emulsion has a pH of greater than about 5.

46. A composition as in claim 1, wherein the aqueous phase is water at a purity level of at least about 95%.

47. A composition as in claim 1, further comprising surfactant present in the emulsion in an amount of not more than about 40 wt % based on the weight of the composition.

48. A composition as in claim 1, further comprising surfactant present in the emulsion in an

amount of not more than about 30 wt % based on the weight of the composition.

49. A composition as in claim 1, further comprising surfactant present in the emulsion in an amount of not more than about 20 wt % based on the weight of the composition.

5

50. A composition as in claim 1, further comprising surfactant present in the emulsion in an amount of not more than about 10 wt % based on the weight of the composition.

51. A composition as in claim 1, further comprising surfactant present in the emulsion in an amount of not more than about 5 wt % based on the weight of the composition.

10

52. A composition as in claim 1 wherein the emulsion has an aqueous content of at least about 20 wt % and includes surfactant in an amount of not more than about 10 wt %.

53. A composition as in claim 1 wherein the emulsion has an aqueous content of at least about 30 wt % and includes surfactant in an amount of not more than about 15 wt %.

15

54. A composition as in claim 1 wherein the emulsion has an aqueous content of at least about 40 wt % and includes surfactant in an amount of not more than about 20 wt %.

20

55. A composition as in claim 1, further comprising a surfactant that is essentially free of nitrogen, sulfur, and phosphorous-containing components.

56. A composition as in claim 1, wherein the composition is stable for at least about 20 microseconds within a temperature range of from about -5° C to about 45° C.

25

57. A composition as in claim 1, wherein the composition is stable for at least about one minute within a temperature range of from about -5° C to about 45° C.

58. A composition as in claim 1, wherein the composition is stable for at least about one hour within a temperature range of from about -5° C to about 45° C.

30

59. A composition as in claim 1, wherein the composition is stable for at least about one day within a temperature range of from about -5° C to about 45° C.

60. A composition as in claim 1, wherein the composition is stable for at least about one month
5 within a temperature range of from about -5° C to about 45° C.

61. A composition as in claim 1, wherein the composition is stable for at least about one year within a temperature range of from about -5° C to about 45° C.

10 62. A composition as in claim 1, wherein the emulsion is stable for at least about one minute within a temperature range of from about -10° C to about 50° C.

63. A composition as in claim 1, wherein the emulsion is stable for at least about one minute within a temperature range of from about -20° C to about 60° C.

15

64. A composition as in claim 1, wherein the emulsion is stable for at least about 10 microseconds at a temperature of at least about 2,000° C.

65. A composition comprising:

20 a mixture of an aqueous phase and a nonaqueous phase, the aqueous phase being present in an amount of at least about 8 wt %, the mixture including a phase boundary area between aqueous and nonaqueous phases of at least about 5 m²/g aqueous phase.

66. A composition as in claim 65, wherein the phase boundary area is at least about 10 m²/g
25 aqueous phase.

67. A composition as in claim 65, wherein the phase boundary area is at least about 15 m²/g aqueous phase.

30 68. A composition as in claim 65, wherein the phase boundary area is at least about 20 m²/g aqueous phase.

69. A composition as in claim 65, wherein the phase boundary area is at least about 25 m²/g aqueous phase.

70. A composition as in claim 65, the mixture including a phase boundary area of at least about
5 50 m²/g mixture.

71. A composition as in claim 65, the mixture including a phase boundary area of at least about 70 m²/g mixture.

10 72. A composition as in claim 65, the mixture including a phase boundary area of at least about 90 m²/g mixture.

73. A composition as in claim 65, wherein the mixture is an emulsion of a discontinuous aqueous phase in a continuous nonaqueous phase, the discontinuous aqueous phase including
15 separate, isolated portions having an average cross-sectional dimension of not more than about 100 nm.

74. A composition as in claim 73, wherein the discontinuous aqueous phase comprises a plurality of aqueous aggregates.

20 75. A kit comprising:

surfactant molecules each including a polar section and a non-polar section, constructed such that when mixed with a composition including a set ratio of an aqueous component and a nonaqueous component they will form an aqueous-in-nonaqueous emulsion including aqueous
25 aggregates of first average cross-sectional dimension in a nonaqueous phase and the surfactant molecules arranged at interfaces between the aqueous aggregates and the nonaqueous phase with the non-polar sections oriented away from the aqueous aggregates into the nonaqueous phase;
and

co-surfactant molecules each including a polar section that is less hydrophilic than the
30 polar section of the surfactant molecules and a non-polar section, constructed such that when mixed with the surfactant molecules and the composition, the co-surfactant molecules are able to insert between the non-polar sections of the surfactant molecules to form aqueous aggregates of a

second cross-sectional dimension less than the first cross-sectional dimension.

76. A kit as in claim 75, wherein the surfactant molecules include polyethylene oxide units and the polar section of the co-surfactant molecules bind to the polyethylene oxide units of the surfactant molecules.

77. A kit as in claim 75, wherein the non-polar section of the surfactant comprises a hydrocarbon chain at least C2 in length.

78. A kit as in claim 75, wherein the non-polar section of the surfactant comprises a hydrocarbon chain at least C4 in length.

79. A kit as in claim 75, wherein the non-polar section of the surfactant comprises a hydrocarbon chain at least C6 in length.

80. A kit as in claim 75, wherein the non-polar section of the surfactant comprises a hydrocarbon chain at least C8 in length.

81. A method comprising:

igniting fuel in the presence of water under conditions in which the water participates in a fuel reforming reaction; and
combusting products of the fuel reforming reaction.

82. A method as in claim 81, the igniting step comprising igniting fuel in the presence of water and a catalyst that catalyzes a fuel reforming reaction.

83. A method as in claim 82, wherein the catalyst is Si, Al, a transition metal, rare earth compound, noble metal, or any oxide, nitride, or carbide of these.

84. A method as in claim 83, wherein the catalyst is a surface of an internal combustion engine.

85. A method of making an aqueous-in-nonaqueous emulsion, comprising:

providing a nonaqueous component;
adding a surfactant system to the nonaqueous component to form a mixture;
alternately adding an aqueous component and a stabilizer to the mixture.

5 86. A method as in claim 85, comprising forming the mixtures via sonication.

87. A method as in claim 85, comprising forming the mixtures via agitation.

88. A method as in claim 85, wherein the stabilizer is less polar than the surfactant.

10

89. A method as in claim 85, wherein the stabilizer is a linear hydrocarbon.

90. A method comprising:

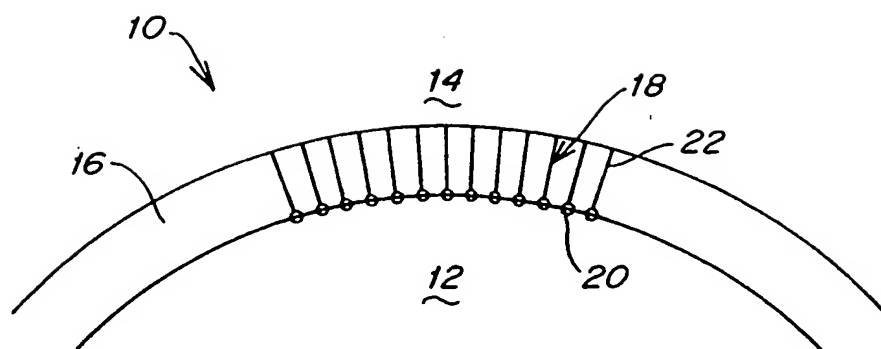
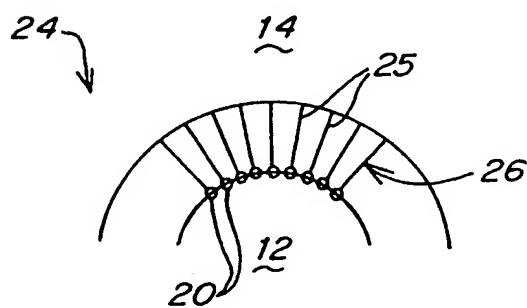
combusting fuel under set conditions in the presence of water, at a temperature lower than
15 that at which the fuel would combust under the set conditions in the absence of water, by creating
radical species at the surface of a catalyst that participate in the combusting step.

91. A method as in claim 90, wherein the catalyst is Si, Al, a transition metal, rare earth
compound, noble metal, or any oxide, nitride, or carbide of these.

20

92. A method as in claim 90, wherein the catalyst is a surface of an internal combustion engine.

1/2

**FIG. 1****FIG. 2**

2/2

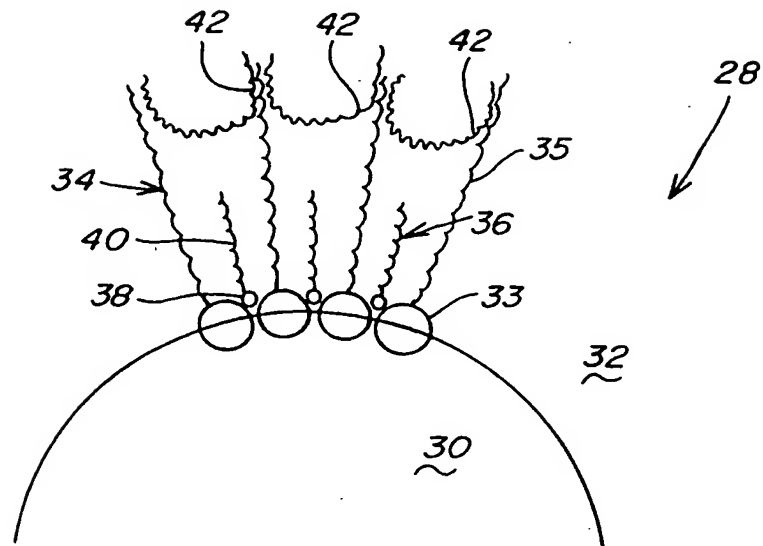
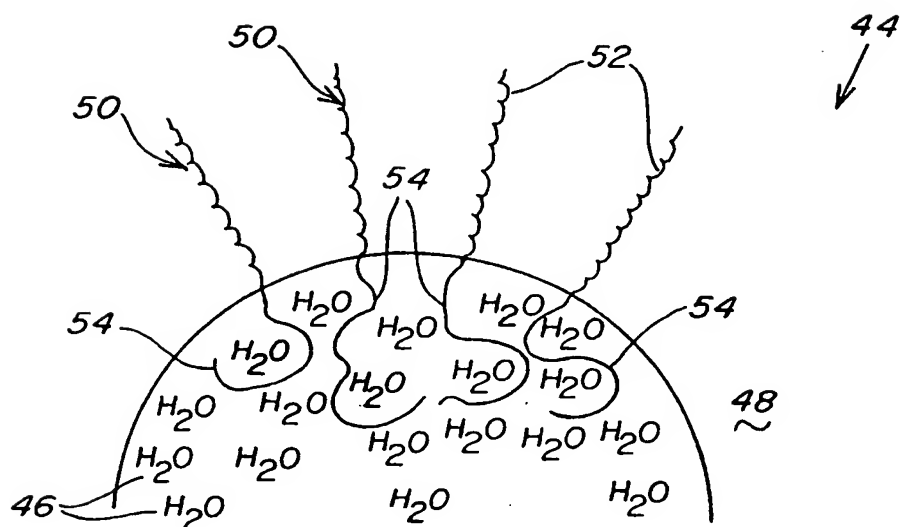
**FIG. 3**

FIG. 4
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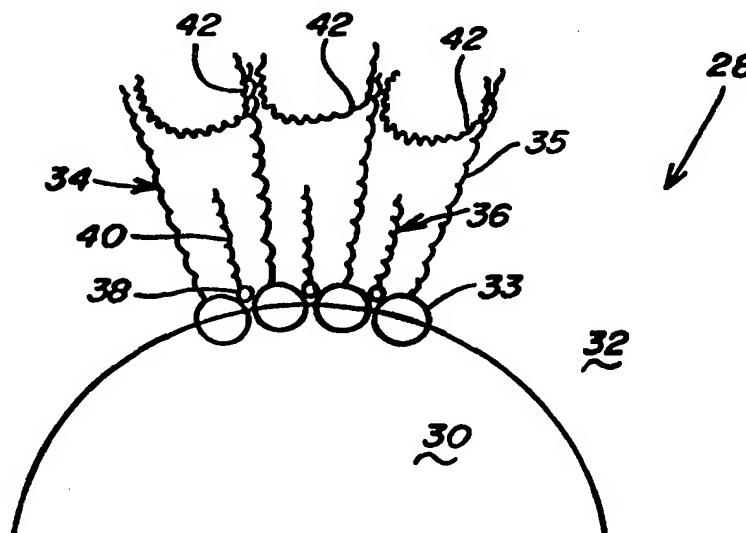


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C10L 1/32	A3	(11) International Publication Number: WO 98/18884 (43) International Publication Date: 7 May 1998 (07.05.98)
(21) International Application Number: PCT/US97/19368 (22) International Filing Date: 28 October 1997 (28.10.97) (30) Priority Data: 08/739,509 28 October 1996 (28.10.96) US (71) Applicant: MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US). (72) Inventors: YING, Jackie, Y.; 9 Fairlane Terrace, Winchester, MA 01890 (US). ZARUR, Andrey; 765 Somerville Avenue #3, Somerville, MA 02143 (US). SUN, Tao; Apartment #220, 4512 N. Saginaw Road, Midland, MI 48640 (US). HEIBEL, Anne, T.; 410 Cliffside Drive, Danville, CA 94526 (US). (74) Agent: OYER, Timothy, J.; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).		(81) Designated States: AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 3 September 1998 (03.09.98)

(54) Title: NANOSTRUCTURED AQUEOUS FUELS**(57) Abstract**

A thermally and temporally-stable water-in-fuel emulsion having micelle size less than 100 nm, and including water in an amount of at least 8 wt.% is provided. The emulsion, when burned as a fuel in an internal combustion engine, exhibits efficient combustion with significantly reduced soot output.



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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/19368

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10L1/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CH 678 283 A (ZUGOL AG) 30 August 1991 see claims 1-4 ---	1,34-40, 47
X A	WO 83 01210 A (PATTERSON WILLIAM P; BAILEY RONALD J) 14 April 1983 see claims 9,10,12 see page 17, line 8 - line 17 ---	1 65,73
X	US 4 394 131 A (MARRO JR JOSEPH ET AL) 19 July 1983 see claims 1-7 ---	1,34,35
A	GB 2 109 405 A (TSAI MAO WU JOHN) 2 June 1983 see claims 1,8 --- -/--	1,34-38

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

23 March 1998

Date of mailing of the international search report

20.07.98

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DE HERDT, O

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/US 97/19368

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 599 088 A (DAVIS MARSHALL E ET AL) 8 July 1986</p> <p>-----</p>	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 97/19368

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

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1-74

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 97/19368

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-74

Emulsion of water aggregates as internal phase in an external non aqueous phase.

2. Claims: 75-80

A kit comprising a surfactant and a co-surfactant for use in an emulsion.

3. Claims: 81-84

Method of igniting a fuel in the presence of water.

4. Claims: 85-89

Method of making an emulsion.

5. Claims: 90-92

Method of combusting a fuel in the presence of water and a dissociating catalyst.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/19368

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